<International Research Center for Elements Science>Advanced Solid State Chemistry

International Research Center for Elements Science – Advanced Solid State Chemistry –

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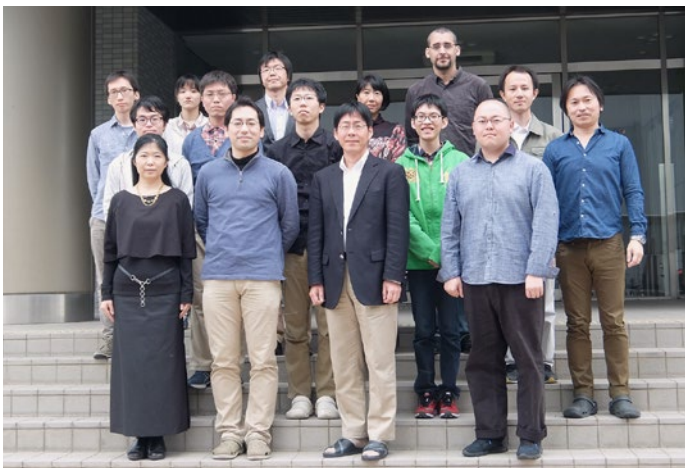
Scope of Research

Transition metal oxides have a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides are used in current electronic devices. Our research mainly focuses on perovskite-structured transition metal oxides with novel functional properties due to complex couplings between their lattices, charges and spins. We are currently exploring such functional oxides with advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth.

KEYWORDS

Solid State Chemistry
Functional Transition Metal Oxides
Epitaxial Thin Film Growth
High Pressure Synthesis
Perovskite Structured Oxides



Selected Publications

Kan, D.; Aso, R.; Sato, R.; Haruta, M.; Kurata, H.; Shimakawa, Y., Tuning Magnetic Anisotropy by Interfacially Engineering the Oxygen Coordination Environment in a Transition-metal Oxide, *Nat. Mater.*, **15,** 432-437 (2016).

Chen, W.-T.; Mizumaki, M.; Seki, H.; Senn, M.; Saito, T.; Kan, D.; Attfield, J. P.; Shimakawa, Y., A Half-metallic A- and B-Site-ordered Quadruple Perovskite Oxide $CaCu_3Fe_2Re_2O_{12}$ with Large Magnetization and a High Transition Temperature, *Nat. Comm.*, **5,** [3909-1]-[3909-7] (2014).

Matsumoto, K.; Haruta, M.; Kawai, M.; Sakaiguchi, A.; Ichikawa, N.; Kurata, H.; Shimakawa, Y., Selective Reduction of Layers at Low Temperature in Artificial Superlattice Thin Films, *Sci. Rep.*, **1,** [27-1]-[27-14] (2011).

Inoue, S.; Kawai, M.; Ichikawa, N.; Kageyama, H.; Paulus, W.; Shimakawa, Y., Anisotropic Oxygen Diffusion at Low Temperature in Perovskite-structure Iron Oxides, *Nat. Chem.*, **2,** 213-217 (2010).

Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y., Temperature-induced A-B Intersite Charge Transfer in an A-Site-ordered $LaCu_3Fe_4O_{12}$ Perovskite, *Nature*, **458,** 60-63 (2009).

Ferromagnetism Induced by Substitution of the Iron(IV) Ion by an Unusual High-Valence Nickel(IV) Ion in Antiferromagnetic $SrFeO_3$

In addition to the usual valence states of 3d transition-metal cations in oxides, such as Fe^{II}/Fe^{III} for Fe and Ni^{II} for Ni, unusual high-valence states, such as Fe^{IV} and Ni^{IV}, can be stabilized in a strongly oxidizing atmosphere. Iron(IV) is stabilized in the cubic perovskite $SrFeO_3$, which is synthesized at high pressure and temperature. The iron(IV) ion in the perovskite, having a nominal d^4 electron configuration in the corner-sharing FeO_6 octahedron, has a spin of S=2, and at low temperatures the compound shows a helical magnetism as a result of competing ferromagnetic and antiferromagnetic interactions between the spins. Ni^{IV}, on the other hand, is stabilized in hexagonal perovskites such as $SrNiO_3$ and $BaNiO_3$ and is expected to have a low spin state (S=0). Indeed, $BaNiO_3$ is nonmagnetic.

In the course of preparing a solid solution of $SrFeO_3$ and $SrNiO_3$, we found that Ni^{IV} is stabilized in the $SrFeO_3$-type cubic perovskite $Sr(Fe^{IV}_{1-x}Ni^{IV}_x)O_3$ with x up to 0.5. Interestingly, the substitution of Fe^{IV} ions by Ni^{IV} ions in the helical antiferromagnetic $SrFeO_3$ induces ferromagnetism with a transition temperature (T_c) higher than room temperature. X-ray absorption spectroscopy and x-ray magnetic circular dichroism spectroscopy imply that substantial magnetic moments of the Ni^{IV} ion were induced by the large magnetic moments of Fe^{IV} through orbital hybridization with oxygen and as a result of this orbital hybridization, ferromagnetism, with the transition temperature above room temperature, is achieved.

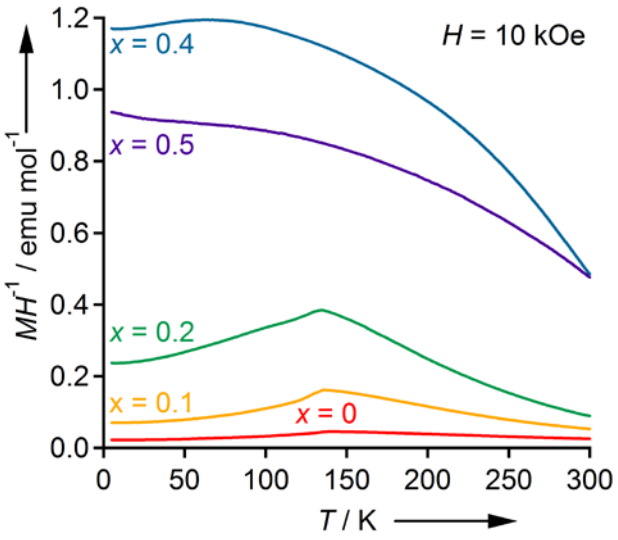


Figure 1. Temperature dependence of magnetic susceptibility for $Sr(Fe_{1-x}Ni_x)O_3$ measured under 10 kOe magnetic field upon heating after zero-field cooling.

Interface Engineering of Oxygen Coordination Environment as a New Route for Exploring Functional Properties of Transition Mental Oxides

The oxygen coordination environments of the transition metals in transition metal oxides often underpin a wide variety of functional properties through crystal field splitting and magnetic interactions. It has been demonstrated that artificial heterostructures and superlattices consisting of dissimilar oxides provide a good platform on which structural distortions associated with changes in metal-oxygen bonds, namely, the oxygen coordination environments, can be engineered. We show that the oxygen coordination environment (or the Ru-O-Ru bond angle) in SRO can be interfacially controlled by inserting a very thin CSTO layer (0-4 monolayers thick) into the SRO/GSO heterointerface. Our aberration-corrected scanning transmission electron microscopy (STEM) observations reveal that the Ru-O-Ru bond angle in the entire SRO layer is controlled through the Ru-O-Ti bond angle, which is determined by the oxygen position at the SRO/CSTO interface. More importantly, the Ru-O-Ti bond angle (or the interfacial oxygen position) can be engineered by layer-by-layer control of the thickness of the CSTO buffer layer that stabilizes the oxygen coordination environment, a Ru-O-Ru bond angle not seen in bulk SRO. Our magneto-transport characterization of the SRO/CSTO/GSO heterostructures also shows that the Ru-O-Ti bond angle plays a decisive role in magnetic anisotropy with the uniaxial magnetic easy axis of the SRO layer, highlighting the significant effect of the interfacially engineered oxygen coordination environment on the spin-orbit interaction of the SRO layer.

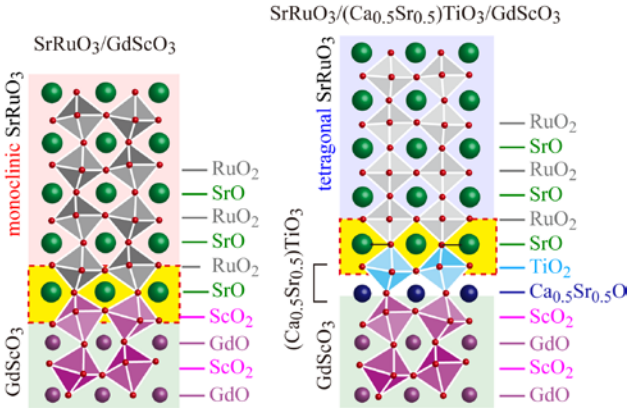


Figure 2. Interface engineering of oxygen coordination environments of perovskite $SrRuO_3$.